Tetrahedron Letters, Vol. 33, No. 37, pp. 5375-5376, 1992
Printed in Great Britain

0040-4039/92 $5.00 + .00
Pergamon Press Ltd

# New Synthetic Route to Ketene Selenoacetals. Reaction of Diethyl 1,1-Bis(phenylseleno)methylphosphonate with Aldehydes and Ketones.

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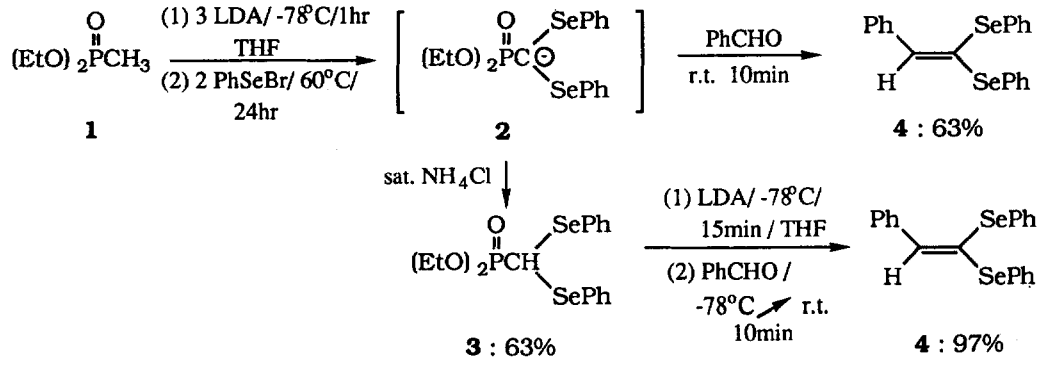
***Abstract:*** *Reaction of 1,1-bis(phenylseleno)methylphosphonate with aldehydes gives ketene selenoacetals quantitatively.*

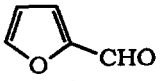
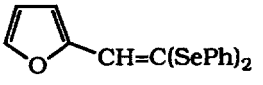
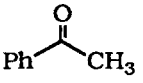
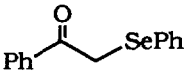
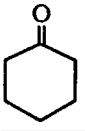
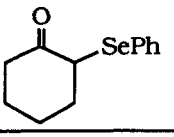
In recent years, the development of a large number of selenium-based synthetic methods has made significant contributions to synthetic organic chemistry.[1] Of special value is the application of selenium methodology to the synthesis of natural products, which often requires highly selective and very efficient transformations.[2] However, few studies of potential synthetic utility of ketene selenoacetals have been published up to now,[3] perhaps due to the lack of an easy high-yield preparation of these compounds. To our knowledge, no preparations have been described in the case of ketene selenoacetals by the direct olefination of carbonyl compounds through Wittig or Horner-Emmons reaction.

We report herein a mild and convenient synthetic method for the preparation of ketene selenoacetals from aldehydes and diethyl 1,1-bis(phenylseleno)methylphosphonate(**3**) as shown in Scheme. The first study for ketene selenoacetals had been done with a one-pot procedure by adding 1eq. PhCHO to the initially formed diethyl 1,1-bis(phenylseleno)methylphosphonate anion(**2**), which gave 63% β,β-bis(phenylseleno)styrene(**4**). This was the same yield that of diethyl 1,1-bis(phenylseleno)methylphosphonate(**3**) from **1**, which means that diethyl 1,1-bis(phenylseleno)methylphosphonate anion(**2**)




**Scheme**

Table. Reaction of Diethyl 1,1-Bis(phenylseleno)methylphosphonate with Aldehydes and Ketones

| Entry | Compound | Product[a] | Yield(%)[b] |
|---|---|---|---|
| 1 | PhCHO | $PhCH=C(SePh)_2$ | 97 |
| 2 | $4\text{-}MeOC_6H_4CHO$ | $4\text{-}MeOC_6H_4CH=C(SePh)_2$ | 95 |
| 3 | $4\text{-}NO_2C_6H_4CHO$ | $4\text{-}NO_2C_6H_4CH=C(SePh)_2$ | 96 |
| 4 | $CH_3(CH_2)_5CHO$ | $CH_3(CH_2)_5CH=C(SePh)_2$ | 95 |
| 5 | PhCH=CHCHO | $PhCH=CHCH=C(SePh)_2$ | 94 |
| 6 |  |  | 94 |
| 7 |  |  | 79 |
| 8 |  |  | 64 |

[a]Products are obtained by preparative thin-layer chromatography.
[b]Isolated yields.

reacted with aldehydes quantitatively.

A typical experimental procedure is as follows: To a stirred solution of LDA(1.0 mmol in 3 ml THF) is added diethyl 1,1-bis(phenylseleno)methylphosphonate (1.0 mmol in 2 ml THF) at -78°C under nitrogen atmosphere. After being stirred for 20 min at the same temperature, benzaldehyde (1.0 mmol in 2 ml THF) is added and the reaction mixture is warmed to room temperaure for 20 min. Then, sat. $NH_4Cl$ solution (5 ml) is added and the mixture is extracted with ether (3 x 20 ml). The combined organic extract is dried ($MgSO_4$) and evaporated to give a β,β-bis(phenylseleno)styrene, which is purified by short-path column chromatography on silica gel or preparative thin-layer chromatography (ether/hexane = 1/20).

With enolizable ketones, the reaction gives an unexpected result that the major product is not a ketene selenoacetal but 2-phenylselenoketone (Entry 7, 8). This result is similar to the behavior which has been observed in the reaction of α-phenylselenophosphorane with ketones.[4]

## REFERENCES


1. Nicolaou, K. C.; Petasis, N. A. *Selenium in Natural Products Synthesis*; CIS, Philadelphia, 1984.
2. Denis, J. N.; Krief, A. *Tetrahedron Lett.* **1982**, 3411.
3. a) Liotta, D. *Organoselenium Chemistry*; John Wiley & Sons, New York, 1987; pp 251-256.
   b) Cristau, H. J.; Chabaud, B.; Labaudiniere, R.; Christol, H. *J. Org. Chem.* **1986**, 51, 875.
4. Petragnani, N.; Comasseto, J. V.; Brocksom, T. J. *J. Organometal. Chem.* **1977**, 124, 1.


(Received in Japan 31 March 1992)